Chemical Kinetics and Transition State Theory
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Lecture 18
Partition Function and equilibrium constant

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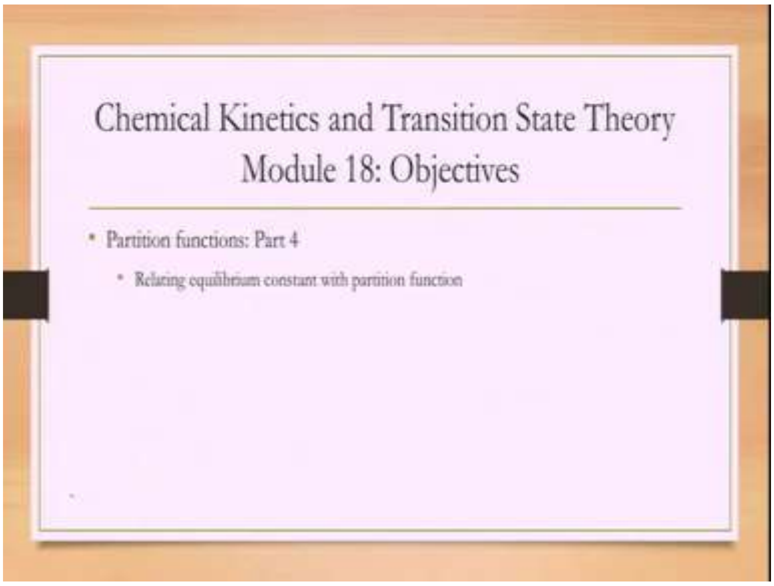

Chemical Kinetics and Transition State Theory
Module 18: Objectives

- Partition functions: Part 4
    - Relating equilibrium constant with partition function

Hello and welcome to Module 18 of Chemical Kinetics and Transition State Theory. In the last few modules, we have been dealing with something called partition functions and they are somewhat technical, somewhat mathematical. But the reason we have been calculating these partition functions is because we needed equilibrium constant.

So, the whole idea that we have is that we want to do transition state theory and the fundamental assumption that transition state theory makes is that the reactants and the transition state is in thermal equilibrium. And if they are in thermal equilibrium, I want to calculate the equilibrium constant between the two; hence I can actually relate the full rate constant with this equilibrium constant.

That is the main idea. So, we have been trying to figure out how to calculate this equilibrium constant and for that we have developed the machinery of partition functions, which is deep within statistical mechanics. So, today we will finally connect, how do we calculate partition functions?

How do we calculate equilibrium constant from partition functions, what we are going to do today is a slightly more ad hoc proof, a much more general proof, you can find an Atkins. So, you can find in this resource. What I am going to cover today is also from Atkins, but slightly more easier to understand proof.

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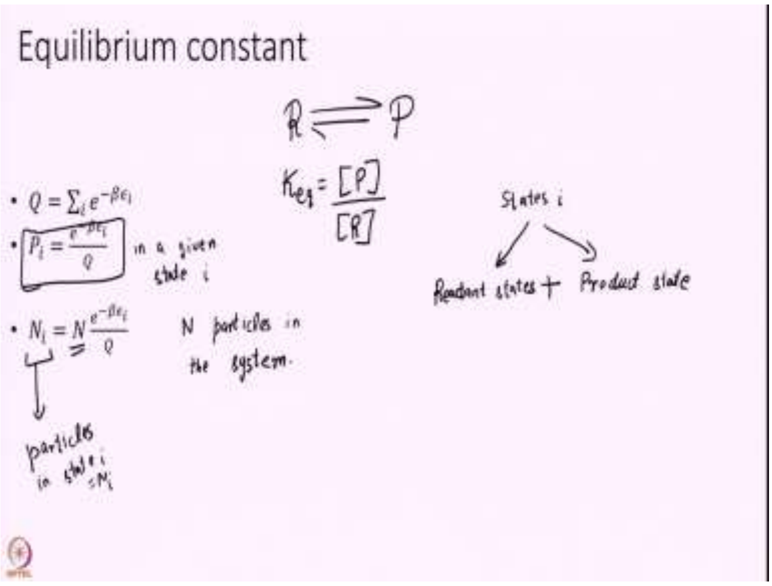

Equilibrium constant

$$R \rightleftharpoons P$$

$$K_{eq} = \frac{[P]}{[R]}$$

- $Q = \sum_i e^{-\beta \epsilon_i}$
- $\boxed{P_i = \frac{e^{-\beta \epsilon_i}}{Q}}$ in a given state i
- $\underbrace{N_i}_{\downarrow} = \underset{\Rightarrow}{N} \frac{e^{-\beta \epsilon_i}}{Q}$ N particles in the system.

particles in state i $= N_i$

States i

Reactant states + Product state

So, what we are really trying to calculate. So let us imagine I have a reaction, some reactant and some product and I want to calculate the equilibrium constant. That will be given by concentration of products divided by the concentration of react. Of course, if you stoichiometric coefficient and all you can put in those stoichiometric coefficient here as well but to understand the idea.

And so the question is how do I relate it to partition functions. So, the point is the following my probability of being in a given state quantum mechanically is given by this formula that is what we discuss in the last module your population in a given state i, you get an e to the power of minus beta ei over q.

So, let us say I have N particles total system, then what is the total number of particles in state i is equal to let us say an Ni, well that will be simply the total number of atoms into the probability that I am in this state. So, now what we do is, we divide our states into two parts, we say some of the states are representative or reactant states and some of the states are representing product states. So, each state is either a reactant state or a product state.

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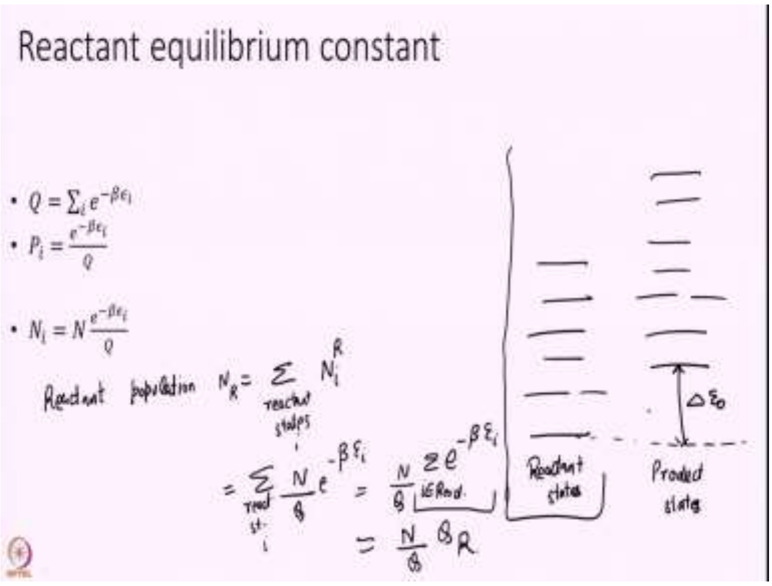

Reactant equilibrium constant

- $Q = \sum_i e^{-\beta \epsilon_i}$
- $P_i = \frac{e^{-\beta \epsilon_i}}{Q}$
- $N_i = N \frac{e^{-\beta \epsilon_i}}{Q}$

Reactant population $N_R = \sum_{\substack{\text{reactant} \\ \text{states} \\ i}} N_i^R$

$$= \sum_{\substack{\text{react} \\ \text{st.} \\ i}} \frac{N}{Q} e^{-\beta \varepsilon_i} = \frac{N}{Q} \underbrace{\sum_{i \in \text{React.}} e^{-\beta \varepsilon_i}}$$

$$= \frac{N}{Q} Q_R$$

So now, I asked you the question, what is the reactant equilibrium constant? So, what we are going to do is we think of these states, I need my pen. So, let us say I have some reactant state somehow. So, these are reactant states and similarly I have made a difference. So, I have a product states as well and there might be degeneracy as well. These are product states.

I have intentionally kept a little bit of a gap between the ground states, which is your exothermic basically. So, the delta e naught is the difference between the product ground state minus react and ground state. So, every state I have put either on this bin of reactants or in the bin of products.

So, let me ask a question, what is the reactant population NR? Well this is nothing but a sum over all reactant states i, Ni so I am only counting over this and that will give me the reactant population. So, this will be equal to sum over reactant states Ni is N over Q e to the power of minus beta, ei, N and Q are independent of i. So, I take it out. So, I will just write this as i belonging to reactant, e to the power of minus beta here.

So, I am simply summing over all those states that are reactants only and not products. So, well this is equal to N over Q and what you notice is, this is nothing but Q, R. So, that is simply the reactant partition function, sum over all levels of the reactants, e to the power of minus beta ER.

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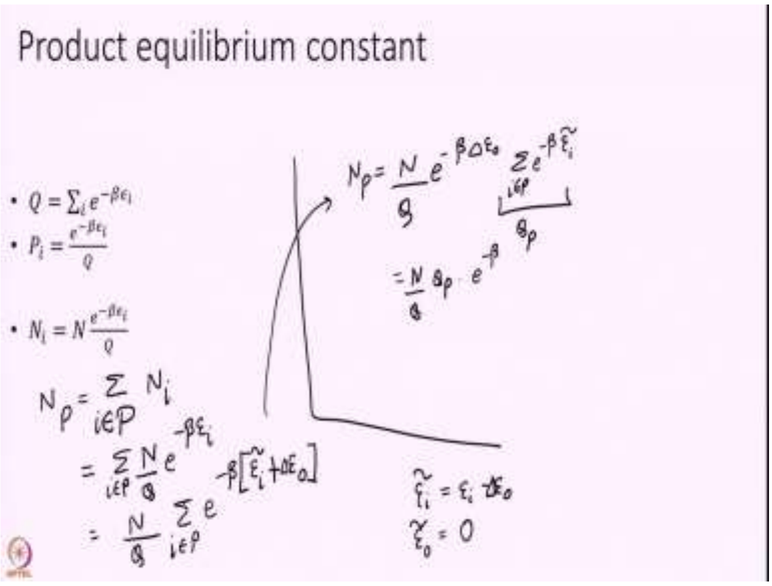

Product equilibrium constant

- $Q = \sum_i e^{-\beta\epsilon_i}$
- $P_i = \frac{e^{-\beta\epsilon_i}}{Q}$
- $N_i = N\frac{e^{-\beta\epsilon_i}}{Q}$

$$N_p = \sum_{i\in P} N_i = \sum_{i\in P}\frac{N}{Q}e^{-\beta\epsilon_i} = \frac{N}{Q}\sum_{i\in P} e^{-\beta[\tilde{\epsilon}_i + \Delta\epsilon_0]}$$

$$N_p = \frac{N}{Q}e^{-\beta\Delta\epsilon_0}\underbrace{\sum_{i\in P} e^{-\beta\tilde{\epsilon}_i}}_{Q_p} = \frac{N}{Q}Q_p\, e^{-\beta}$$

$\tilde{\epsilon}_i = \epsilon_i - \Delta\epsilon_0$

$\tilde{\epsilon}_0 = 0$

So, we will do the same analysis for products now. So, NP is sum over all i that belongs to only product states, Ni and this is equal to sum over i belonging to only product N over Q, e to the power of minus beta ei and i belonging to product, but there is a little trick here, what I will do is, I will write this as N over Q Of course I take out, I will write this as I over product, e to the power of minus beta ei tilde minus e 0, plus e 0, where ei tilde is ei minus ei naught, this is delta e naught.

So, delta e naught that is the difference here is I have just subtracted it out and the reason I do that is once more the partition function by convention; I define it so that the ground state energy is 0. So, the point is e0 is equal to 0, e0 tilde. So, I take this and this is equal to NP is equal to N over Q, E to the power of minus beta delta e naught also comes out and you get sum over i belonging to product, e to the power of minus beta ei tilde and this is your QP. So, you get N over Q QP into e to the power of minus beta delta e naught

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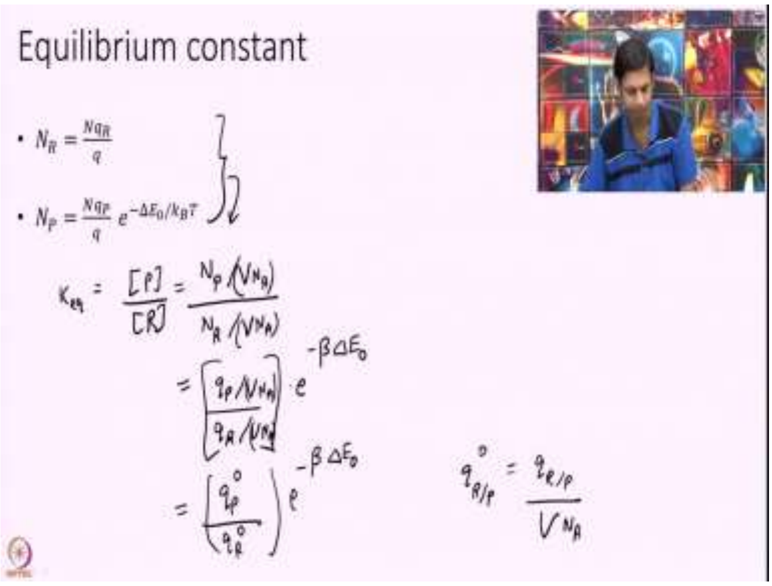

Equilibrium constant

- $N_R = \frac{N q_R}{q}$
- $N_P = \frac{N q_P}{q} e^{-\Delta E_0 / k_B T}$

$$K_{eq} = \frac{[P]}{[R]} = \frac{N_P / (V N_A)}{N_R / (V N_A)}$$

$$= \left[\frac{q_P / V N_A}{q_R / V N_A}\right] \cdot e^{-\beta \Delta E_0}$$

$$= \left(\frac{q_P^0}{q_R^0}\right) e^{-\beta \Delta E_0}$$

$$q^0_{R/P} = \frac{q_{R/P}}{V N_A}$$

So, I have my NR and NP Now, how do I again calculate my reactant by equilibrium constant. So, my equilibrium constant is concentration of P divided by concentration of R, but concentration of P is nothing but the number of P divided by volume divided by N of R divided by volume. So, you can also put the Avogadro number in here if you want this I am writing in atomic numbers.

So, I put NP and NR from here and you will notice that N over Q will cancel out. So, what I will end up with is qp over volume divided by qr over volume into e to the power of minus beta delta E naught and we simply call these as qp naught and qr just so that it is easier for me to write. Where qR or P naught is simply qR or qP divided by the volume.

So, this is per unit volume and if you are more careful you also divide by Avogadro number if you want it in moles. So, I will be a slightly more careful and divided by moles as well and so I defined divided by NA here as well and so this becomes per mole. So, that depends on the problem basically what you are, in what unit you are trying to solve the problem here.

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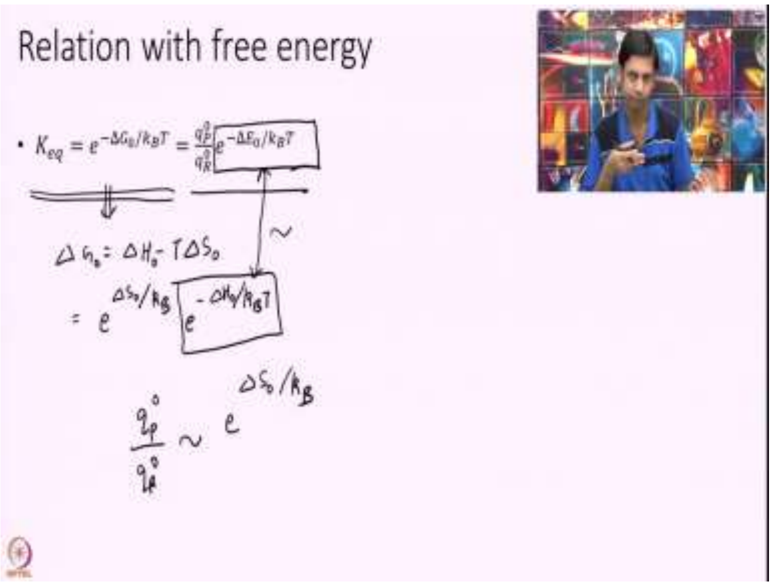

Relation with free energy

- $K_{eq} = e^{-\Delta G_0/k_BT} = \frac{q_P^0}{q_R^0}\boxed{e^{-\Delta E_0/k_BT}}$

$\Delta G_0 = \Delta H_0 - T\Delta S_0$

$= e^{\Delta S_0/k_B}\boxed{e^{-\Delta H_0/k_BT}}$

$\sim$

$\frac{q_P^0}{q_R^0} \sim e^{\Delta S_0/k_B}$

Finally, I just want to point out one interesting observation. If you know your thermodynamics a little bit you will know that this is an equation that Gibbs had given. That the equilibrium constant is also related to free energy and right now we have argued this is equal to this relation or in terms of partition functions.

So, let us just analyse this a little bit, let us massage this a little bit. So, this we get delta G naught if you remember is delta H naught minus T delta S. So, we put it here and what we get is e to the power of I will just write it in a form that is compares with the partition function form.

So, I have written this entropy part first and cancelled the temperature and then the enthalpy part and so the point that I want to bring about is the following, it is a qualitative comparison, this portion here actually relates with this portion here, are they are not equal, but the point is delta H naught and delta E naught are usually related by difference of RT or 2RT or kBT in this language

So, these two terms are related to each other. More interestingly the term of partition functions relates with the entropy term. So, this you should remember that the partition functions correlate with entropy and the energy part relates with enthalpy to a factor. There is always that RT term that will be there. So, that is just a comment I wanted to bring about for what we have discovered.

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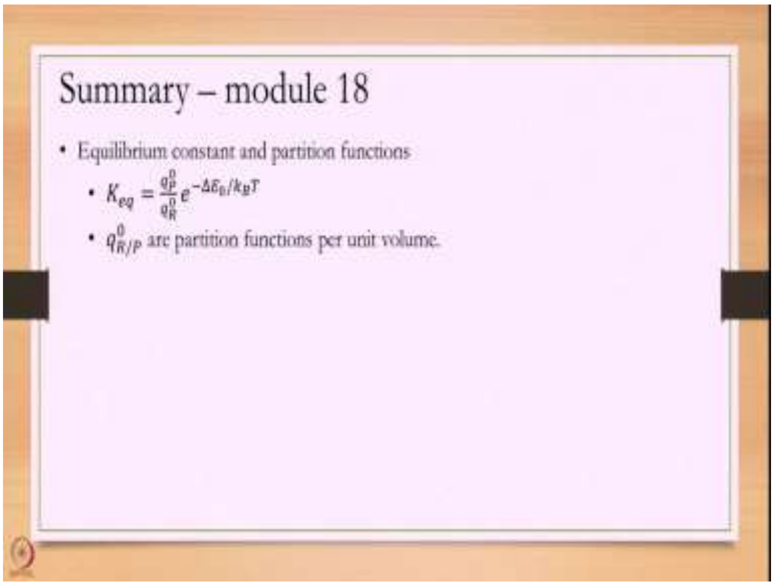

Summary – module 18

- Equilibrium constant and partition functions
  - $K_{eq} = \frac{q_P^0}{q_R^0} e^{-\Delta E_0/k_B T}$
  - $q_{R/P}^0$ are partition functions per unit volume.

So, in summary today we have looked at the relation of equilibrium constant in terms of partition functions. So, this is the formula that we have derived today. A more rigorous formula you can look into Atkins and these partition functions that we have calculated are really partition functions per unit volume and per divided by Avogadro number as well, if you are looking into a molar units. Thank you very much.